# LIGHT SCATTERING STUDIES ON POLYELECTROLYTES

BY

MARSHALL RAYMOND HATFIELD

B.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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## Introduction

A beam of light passing through a gaseous or liquid system forces loosely bound electrons in the material to vibrate. Light is then emitted in all directions in the form of scattered radiation generally with the frequency unchanged from that of the incident light. Shape, size and interactions of the molecules in the material determine the intensity and distribution of the scattered radiation. Conversely, a knowledge of the light scattering properties of a system can lead to a quantitative measurement of shape and size of the molecules of that system.

Light scattering could be applied to an extensive variety of problems but has been particularly useful in the determination of molecular weights and particle sizes of polymers. Since polyelectrolyes are high polymers which are capable of ionizing to some extent in polar solvents they exhibit many unusual properties. In aqueous solution these materials are charged, the magnitude of which depends upon the extent of ionization. Changes in charge result in size variation because of the electrostatic forces involved. Light scattering affords a relatively simple method by which these size changes may be studied.

Molecular weights of polyelectrolytes can be determined by the light scattering techniques used for homopolar polymers (1) (2) (3) (4) (5) providing the polymeric electrolyte is suitably soluble in some non-ionizing solvent. Aqueous solutions, however, present intriguing problems resulting from the above mentioned size changes. This investigation is primarily a study of such solutions.

## Results

The relationship between turbidity and molecular weight

is expressed by the Debye equation for small particles (ie. particles of a size less than 1/10 of the wavelength of light used) which can be written

$$(Hc/t)_0 = 1/M$$

where H is a constant for a particular polymer-solvent system dependent only upon the refractive index and wavelength, c the concentration, t the turbidity, and M the weight average molecular weight. The subscript zero indicates the value of the expression obtained by extrapolation to infinite dilution.

When Hc/t is plotted against concentration for homopolar polymers a straight line results which is easily extrapolated to zero concentration. Since polyelectrolyte molecules are charged in aqueous solutions, peculiar scattering curves are obtained which are difficult to interpret. By utilization of buffer solutions as solvents to hold the molecular size constant, the difficulties involving the interpretation of scattering data were resolved. The weight average molecular weight of two polymeric acids was determined by a 90° scattering method.

The average molecular weight of a particular sample of polyacrylic acid at pH values of 1.2, 3, 4, and 5 was found to be 206,000 ± 10%. Molecular weight values at a particular pH using a specific buffer were reproducible to about ± 3% The remainder of the error was attributed to association of buffer ions with the charged polymer. The size of the particles in solution was found to be less than about 550 A in the low pH regions with a definite tendency to increase at higher pH values. The slope of the straight line obtained when the reciprocal specific scattering was plotted against concentration was shown to be dependent upon pH. This dependence of slope was noticeably related to particle size and shape.

Polyacrylic acid is insoluble in most aromatic hydrocarbons but is soluble in absolute ethanol. Since this is a non-ionizing solvent, even a polyelectrolyte in such a solution exhibits scattering behavior typical of un-ionized polymers. The molecular weight under these conditions was found to be 206,000, in sub-

stantial agreement with values obtained in buffer solvents.

A copolymer of maleic acid and styrene was studied in the same manner with similar, but not as conclusive, results. The average molecular weight of this material for pH values of 3, 4, and 5 was 164,000 $\pm$ 15%. The particle size at all pH values was small compared to the wavelength of the light used but in other respects, such as the slope of the scattering curves, the material was similar to polyacrylic acid.

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## VITA

The author was born on December 26, 1923, in Kansas City, Missouri. He attended a local high school and, in 1940, entered the Junior College of Kansas City. After graduating, he registered at the University of Illinois in the curriculm of Chemical Engineering. In 1943 he was called to active duty in the United States Naval Reserve and served with the fleet in the Pacific and Atlantic Oceans until 1946. He re-entered the University of Illinois and received the degree of Bachelor of Science in Chemical Engineering in June, 1947. The following September he enrolled in the Graduate College and has held a Research Assistantship in Chemistry on the U.S. Government Rubber Research Program since September, 1948. The author is a member of Sigma Xi, Phi Lambda Upsilon, Tau Beta Pi, Sigma Tau, and Alpha Chi Sigma.

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